



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Sequential, Kinetically Controlled Synthesis of Multicomponent Stereoisomeric Assemblies

Citation for published version:

Chepelin, O, Ujma, J, Barran, PE & Lusby, PJ 2012, 'Sequential, Kinetically Controlled Synthesis of Multicomponent Stereoisomeric Assemblies', *Angewandte Chemie International Edition*, vol. 51, no. 17, pp. 4194-4197. <https://doi.org/10.1002/anie.201108994>

Digital Object Identifier (DOI):

[10.1002/anie.201108994](https://doi.org/10.1002/anie.201108994)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

Angewandte Chemie International Edition

Publisher Rights Statement:

Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



This is the peer-reviewed version of the following article:

Chepelin, O., Ujma, J., Barran, P. E., & Lusby, P. J. (2012). Sequential, Kinetically Controlled Synthesis of Multicomponent Stereoisomeric Assemblies. *Angewandte Chemie-International Edition*, 51(17), 4194-4197.

which has been published in final form at <http://dx.doi.org/10.1002/anie.201108994>

This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for self-archiving (<http://olabout.wiley.com/WileyCDA/Section/id-817011.html>).

Manuscript received: 20/12/2011; Article published: 05/03/2012

Sequential, Kinetically Controlled Synthesis of Multicomponent Stereoisomeric Assemblies**

Oleg Chepelin,¹ Jakub Ujma,¹ Perdita E. Barran^{1,*} and Paul J. Lusby^{1,*}

^[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

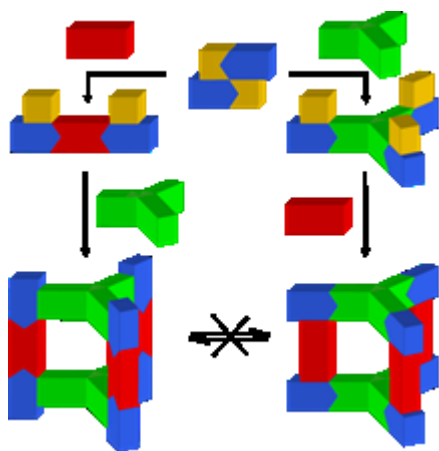
^[*]Corresponding author; P.J.L. e-mail: Paul.Lusby@ed.ac.uk; homepage: <http://www.chem.ed.ac.uk/staff/academic/lusby.html>; P.E.B. e-mail: Perdita.Barran@ed.ac.uk, homepage: <http://homepages.ed.ac.uk/pbarran/PBRG/>

^[**]This work was supported by the EPSRC and the Royal Society. P.J.L. is a Royal Society University Research Fellow.

Supporting information:

For full synthetic details and compound characterisation, see the Supporting Information; available on the WWW under <http://www.angewandte.org> or from the author.

Graphical abstract:



Keywords:

cyclometalated complexes; kinetic control; platinum; self-assembly; supramolecular chemistry

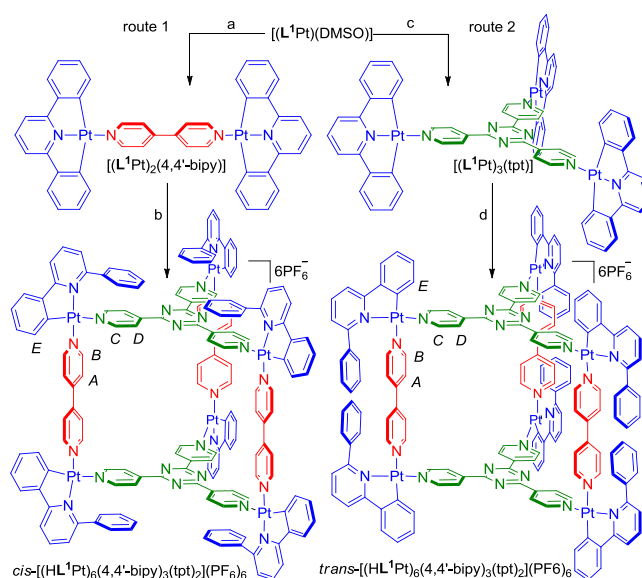
Abstract

The vast difference in labilities of *cis*-exchangeable platinum coordination sites has been exploited to selectively synthesise multicomponent stereoisomeric assemblies using a template-free, sequential, kinetically controlled approach.

Main text

The reversibility of non-covalent and metal ligand interactions has widely been exploited to synthesise a plethora of supramolecular and coordination based assemblies under thermodynamic control.^[1] Occasionally, entrapment in local energy minima leads to the formation of metastable products, which are often converted into lower energy products upon prolonged reaction times.^[2] In contrast, self-assembled products in Nature almost always arise according to the most expedient reaction pathway, rather kinetically selected.^[3] Here we demonstrate a kinetically-controlled approach to self-assembly in which the sequence of addition^[4] of molecular tectons leads to the stereoselective formation of metallosupramolecular isomers.

The use of platinum(II) (and other 3rd row TMs) is particularly well suited to a kinetic approach to self-assembly, not just because Pt ligand bonds can be kinetically inert, but also because the metal ion can be conveniently tuned to produce a vast range of different ligand exchange labilities. For instance, assemblies which utilise *bis*-phosphine ligands as corner protecting groups often readily assemble at room temperature,^[5] while those which exploit neutral *N*-donor bidentate ligands, such as ethylene diamine, typically require several hours at elevated temperature to reach equilibrium.^[6] Furthermore, the mechanism of labilisation, *i.e.* the trans effect, is such that it is possible for a single metal centre to possess *cis* exchangeable sites with dramatically different kinetic properties. We have recently prepared a metallosupramolecular trigonal prism that possesses an unsymmetrical cyclometallated C[∧]N corner protecting group, which was assembled in two steps by treating [$\text{L}^1\text{Pt}(\text{DMSO})$] (where $\text{H}_2\text{L}^1 = 2,6\text{-diphenylpyridine}$) sequentially with 4,4'-bipy and tpt.3CSA (where tpt = tris(4-pyridyl)triazine and CSA = camphorsulfonic acid) (Scheme 1, steps a and b).^[7] The isolation of a single isomeric product from a possible fourteen, as indicated by the ^1H NMR spectrum of the hexa- PF_6 salt (Figure S1a; see Supporting Information), led us to ask was this selectivity due to each Pt centre possessing one labile and one inert exchangeable site, or was the selectivity thermodynamic in origin?



Scheme 1. Sequence specific control over the formation of metallosupramolecular stereochemical isomers. a) 4,4'-bipy, CH₂Cl₂, rt, 18 h, 77%; b) (i) tpt.3CSA, CH₂Cl₂, rt, 1 h; (ii) NH₄PF₆, 97%; c) tpt, CH₂Cl₂, 18 h, 85%; d) (i) 4,4'-bipy.2CSA, CH₂Cl₂, rt, 3 h; (ii) NH₄PF₆, 99%.

To answer this, the sequence in which 4,4'-bipy and tpt were added to [L¹Pt(DMSO)] was reversed. [L¹Pt(DMSO)] was first reacted with a third of an equivalent of tpt at room temperature in CH₂Cl₂ to give [(L¹Pt)₃(tpt)] (Scheme 1, step c), which was then treated with 4,4'-bipy.2CSA, and following metathesis with NH₄PF₆, the hexa-PF₆ salt was isolated in 99% yield (Scheme 1, step d). The ¹H NMR spectrum of this product (Figure S1b; see Supporting Information) also indicated the formation of a single species, yet clear differences between the isomers, in particular, to resonances H_{A-E} could be observed. The absolute assignment of the two products as *cis* and *trans*-[(HL¹Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆ from routes 1 and 2, respectively, has been made on the basis that (a) the *ortho* resonance of tpt (H_C) is more deshielded in the *trans*-to-nitrogen coordination site in comparison to 4,4'-bipy (H_B), and (b) the large and small relative separations between the H_A/H_B and H_C/H_D pairs, respectively.

To corroborate the solution assignment, analysis was undertaken using nanoelectrospray mass spectrometry (n-ESI). While samples of the presumed *cis*- and *trans*-isomers both showed peaks which matched the predicted isotope pattern for the intact 3+ and 2+ cages (1360 and 2114 *m/z* respectively), their collision induced dissociation (CID) pathways differed significantly. For instance, MS-MS experiments showed that with increasing kinetic energy, the isolated intact 3+ cage [(HL¹Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₃]³⁺ from the *cis* isomer initially fragments to give ions at 1308 and 1464 *m/z*, which then fragments further to a dominant species at 1152 *m/z* (Figure 1a). Although the singly charged peak at 1152 *m/z* unambiguously corresponds to [(HL¹Pt)₂(4,4'-bipy)]PF₆]⁺, and thus supports the assignment of the *cis* isomer in which the weaker *trans*-to-phenylato Pt-tpt bond undergoes selective dissociation at lower potential, the peaks at both 1308 (+2) and

1464 (+1) m/z could correspond to more than one different structure with the formulas $[(\text{HL}^1\text{Pt})_4(4,4'\text{-bipy})_2(\text{tpt})](\text{PF}_6)_2]^{2+}$ and $[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})(\text{tpt})](\text{PF}_6)]^+$, respectively. However, further MS³ experiments with both the species at 1308 and 1464 m/z showed the predominant appearance of the +1 ion at 1152 m/z ($[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})](\text{PF}_6)]^+$). This suggests that the ions at 1308 and 1464 m/z correspond to tpt coordinated with two and one $[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})]$ unit(s) and that initial fragmentation of the cage results from cleavage of Pt-tpt bonds from adjacent panels (Figure 1a, inset). When the isolated 3+ ion from the *trans* isomer was subjected to the same CID experiment, a signal at 1308 m/z was also observed at low voltage (Figure 1b), yet the different charge state (+3) indicates that the initial fragmentation involves the loss of a single 4,4'-bipy ligand to give $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_2(\text{tpt})_2](\text{PF}_6)_3]^{3+}$ (Figure 1b, inset). At higher potential, this peak diminishes with a concomitant appearance of a +2 ion at 866 m/z , which unequivocally corresponds to $[(\text{HL}^1\text{Pt})_3(\text{tpt})]^{3+}$. This fits with a preferential, low energy dissociation of the weaker Pt-4,4'-bipy bond from the *trans* isomer (Figure 1b, inset).

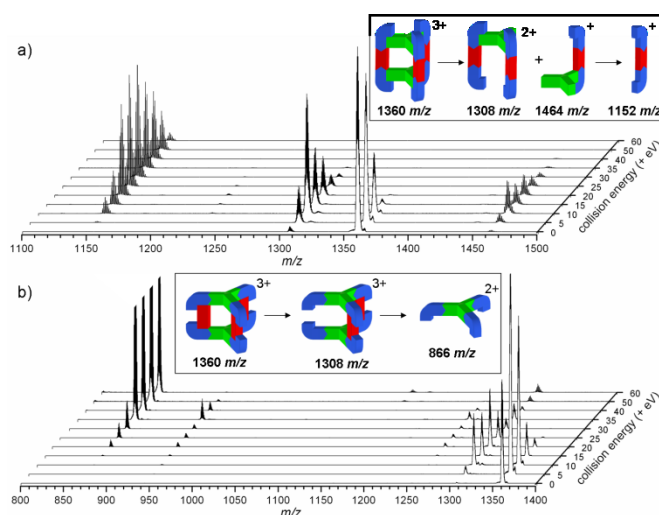
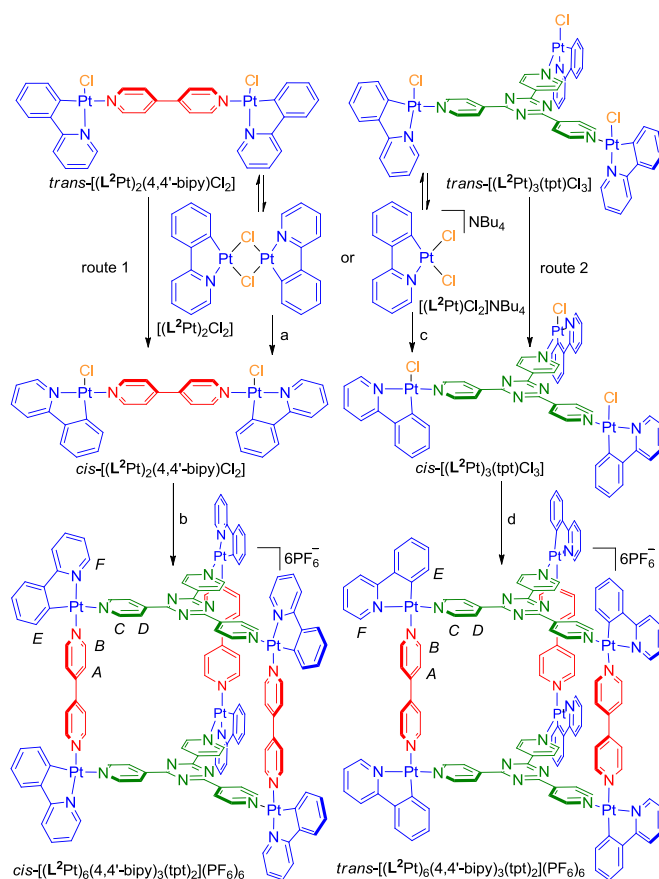


Figure 1. Partial n-ESI spectra with increasing collisional energy of the +3 intact prism (1360 m/z) to illuminate the CID pathways (see insets) for a) *cis* and b) *trans*- $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$.

To ascertain whether a kinetic self-assembly strategy could be used if the labile coordination site isn't initially masked, we have investigated the sequential addition of tpt and 4,4'-bipy to both $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ and $[(\text{L}^2\text{Pt})\text{Cl}_2]\text{NBu}_4$, where HL^2 is the bidentate C[^]N ligand 2-phenylpyridine (Scheme 2). The ¹H NMR spectrum of a mixture of $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ and 0.5 equiv. of 4,4'-bipy (Scheme 2, route 1, step a) showed the appearance of several new peaks after 5 minutes (Figure S2b; see Supporting Information) which differed from the $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ starting material (Figure S2a; see Supporting Information). However, the gradual disappearance of these initial peaks and the concomitant appearance of a new set of signals, which converged to a single species after 24 h at 45 °C, was observed (Figure S2c; see Supporting Information). Based on the

relative chemical shifts, and in particular the significant differences of H_E and H_F in the initial and final compounds (which is caused by shielding by the coordinated 4,4'-bipy ligand), it appears that *trans*- $[(L^2Pt)_2(4,4'\text{-bipy})Cl_2]$ is the initial kinetic product, which rearranges into the thermodynamically (and kinetically) more stable *cis*- $[(L^2Pt)_2(4,4'\text{-bipy})Cl_2]$ (Scheme 2, route 1, step a).^[8] Following halide extraction using AgCSA, reaction with tpt and then anion exchange with NH_4PF_6 , *cis*- $[(L^2Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$ was isolated in virtually quantitative yield (Scheme 2, route 1, step b). The 1H NMR spectrum of this product (Figure S2d; see Supporting Information) again suggested the formation of a single isomer. When the sequence of addition of 4,4'-bipy and tpt to $[(L^2Pt)_2Cl_2]$ was switched (Scheme 2, route 2) a single, yet different product was obtained. A comparison of the 1H NMR spectra of the two isomers showed significant differences (Figures S2d and S2e; see Supporting Information), particularly in resonances H_{A-F} .



Scheme 2. Kinetically controlled synthesis using an “unmasked” corner protecting ligand. a) 4,4'-bipy, $C_2H_2Cl_4$, 45 °C, 24 h; b) (i) AgCSA, $C_2H_2Cl_4$, RT, 3 h; (ii) tpt, $C_2H_2Cl_4$, RT, 24 h; (iii) NH_4PF_6 , 98% (starting from $[(L^2Pt)_2Cl_2]$); c) tpt, $C_2H_2Cl_4$, 45 °C, 24 h; d) (i) AgCSA, $C_2H_2Cl_4$, RT, 3 h; (ii) 4,4'-bipy, $C_2H_2Cl_4$, RT, 24 h; (iii) NH_4PF_6 , 77% (starting from $[(L^2Pt)_2Cl_2]$).

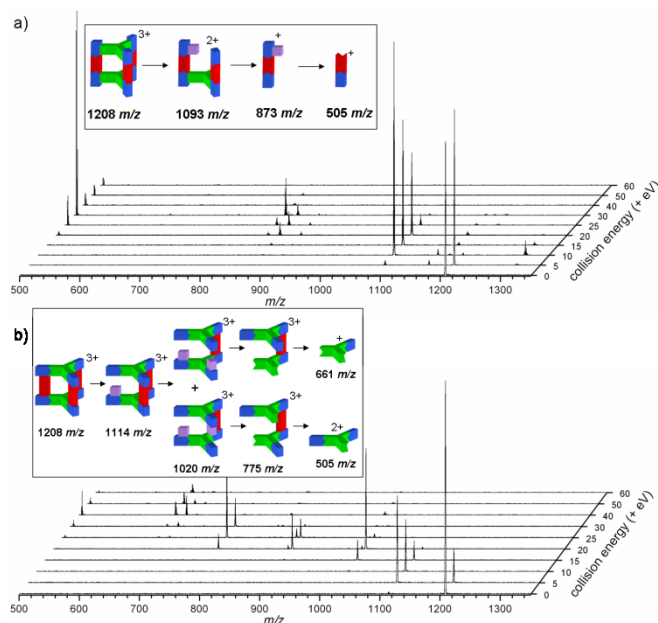


Figure 2. Partial n-ESI mass spectra with increasing collisional energy of the +3 intact prism (1208 m/z) to illuminate the fluoride induced CID pathways (see insets) for a) *cis* and b) *trans*-[(L^2 Pt) $_6$ (4,4'-bipy) $_3$ (tpt) $_2$](PF $_6$) $_6$.

The n-ESI mass spectra of *cis* and *trans*-[(L^2 Pt) $_6$ (4,4'-bipy) $_3$ (tpt) $_2$](PF $_6$) $_6$ showed identical peaks at 1208 and 1884 m/z , which matched the predicted isotope patterns for the intact +3 and +2 prisms, respectively (not shown). However, in contrast to the analogous experiments with *cis* and *trans*-[(HLPt) $_6$ (4,4'-bipy) $_3$ (tpt) $_2$](PF $_6$) $_6$, the CID of the *cis* and *trans*-isomers of L^2 showed mainly peaks that did not correspond to any sensible combinations of L^2 Pt, 4,4'-bipy, tpt and PF $_6$. Instead, the dominant CID pathway for both *cis* and *trans*-[(L^2 Pt) $_6$ (4,4'-bipy) $_3$ (tpt) $_2$](PF $_6$) $_3$] $^{3+}$ involves fluoride abstraction from the PF $_6$ counteranions. With the *cis* isomer, the disappearance of the 1208 m/z peak is initially accompanied by a dominant species at 1093 m/z , which corresponds to the formula [(L^2 Pt) $_4$ (4,4'-bipy) $_2$ (tpt)F](PF $_6$) $_2$] $^{2+}$ (Figure 2a). In an analogous manner to *cis* isomer of L , it appears that the initial fragmentation pathway involves the cleavage of the weaker Pt-tpt bonds from adjacent panels (also supported by a smaller intensity ion at 1311 m/z , which corresponds to [(L^2 Pt) $_2$ (4,4'-bipy)(tpt)PF $_6$] $^{+}$), a route that is either promoted or stabilised by abstraction of fluoride from one of the PF $_6$ counteranions (Figure 2a, inset). MS 3 experiments show that the disappearance of this 1093 m/z ion results from the dissociation into a low intensity ion at 873 m/z , matching [(L^2 Pt) $_2$ (4,4'-bipy)F] $^{+}$, and subsequent MS 4 shows that this fragments into a singly charged ion at 505 m/z , by loss of the neutral [(L^2 Pt)F] from [(L^2 Pt) $_2$ (4,4'-bipy)F] $^{+}$. For the *trans* isomer, the fragmentation pathway appears to first involve loss of a single 4,4'-bipy, again either promoted or stabilised by fluoride abstraction from the counter anion, to give [(L^2 Pt) $_6$ (4,4'-bipy) $_2$ (tpt) $_2$ F](PF $_6$) $_2$] $^{3+}$ (1114 m/z), which subsequently loses another 4,4'-bipy via a fluoride promoted/stabilised route to produce [(L^2 Pt) $_6$ (4,4'-bipy)(tpt) $_2$ F $_2$](PF $_6$) $_2$] $^{3+}$ (1020 m/z). Again, the selective loss

4,4'-bipy ligands from the weaker *trans*-to-phenylato coordination sites supports the formation of *trans*- $[(L^2Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$.

The four metallocsupramolecular stereochemical isomers do not undergo isomerisation, or reassemble to generate other assemblies (e.g. Pt_4 squares or $Pt_6(tpt)_4$ cages) at room temperature in solution.^[9] We attribute this stability to the unlabile Pt-N bonds *trans* to the nitrogen donors of HL^1/L^2 ; although these bonds form readily at room temperature from the corresponding solvato / halide complexes (or just above in the case of L^2), the activation barrier for de-coordination is such that this step is essentially irreversible under ambient conditions. Therefore the sequence in which the *N*-donor bridging ligands are added to the starting platinum complexes determines the stereochemical outcome of the reaction. In this regard, the synthesis of these metallocsupramolecular isomers combines elements of covalent (irreversible) synthesis and non-covalent (reversible) thermodynamically-controlled assembly. It could also be expected that the isomers would show some thermodynamic bias towards either the *cis* or the *trans* form, however, heating samples of either *cis* or *trans*- $[(HL^1/L^2Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$ at 80 °C for 24 h results in a complex mixture with no obvious preference for a single species. This is perhaps unsurprising as to gain greater than 95% selectivity for a single species, an energy difference greater than 1.74 kcal mol⁻¹ would be required. This is in marked contrast to the sequential, kinetically-controlled synthesis described here, which give greater than 95% selectivity for single stereochemical isomers, highlighting the potential benefits of exploiting differences in rates of assembly, rather than simply considering ground state energies, for the preparation of multicomponent systems.

The vast difference in labilities of *cis*-exchangeable platinum coordination sites have been exploited to selectively synthesise multicomponent stereoisomeric assemblies using a template-free, sequential, kinetically controlled approach. We anticipate that this approach to non-covalent, and in particular coordination driven self-assembly will facilitate the generation of multicomponent, ultimately functional systems.

Notes and references

- [1] For recent examples, see a) Q.-Fu Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, 328, 1144-1147; b) M. Wang, Y.-R. Zheng, K. Ghosh, P. J. Stang, *J. Am. Chem. Soc.* **2010**, 132, 6282-6283; c) S. Hiraoka, M. Kiyokawa, S. Hashida and M. Shionoya, *Angew. Chem.* **2010**, 122, 142-147; *Angew. Chem. Int. Ed.* **2010**, 49, 138-143; d) C. J. Hastings, M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2010**, 132, 6938-6940; e) T. Liu, Y. Liu, W. Xuan, Y. Cui, *Angew. Chem.* **2010**, 122, 4215-4128; *Angew. Chem. Int. Ed.* **2010**, 49, 4121-4124; f) A. Kaloudi-Chantzea, N. Karakostas, C. P. Raptopoulou, V. Psycharis, E. Saridakis, J. Griebel, R. Hermann, G. Pistolis, *J. Am. Chem. Soc.* **2010**, 132, 16327-16329; g) J. Dömer, J. C. Slootweg, F. Hupka, K. Lammertsma, F. E. Hahn, *Angew. Chem.* **2010**, 122, 6575-6578; *Angew. Chem. Int. Ed.*, **2010**, 49, 6430-6433; h) K. E. Allen, R. A. Faulkner, L. P. Harding, C. R. Rice, T. Riis-Johannessen, M. L. Voss, M. Whitehead, *Angew. Chem.* **2010**, 122, 6805-6808; *Angew. Chem. Int. Ed.*, **2010**, 49, 6655-6658; i) X. Kuang, X. Wu, R. Yu, J. P. Donahue, J. Huang, C.-Z. Lu, *Nature Chem.* **2010**, 2, 461-465; j) M. Beyler, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **2010**, 132, 4409-4417; k) J.-R. Li, H.-C. Zhou, *Nature Chem.* **2010**, 2, 893-898; l) J. L. Atwood, E. K. Brechin, S. J. Dalgarno, R. Inglis, L. F. Jones, A. Mossine, M. J. Paterson, N. P. Power, S. J. Teate, *Chem. Commun.*, **2010**, 46, 3484-3486; m) S. Perera, X. Li, M. Soler, A. Schultz, C. Wesdemiotis, C. N. Moorefield, G. R. Newkome, *Angew. Chem.* **2010**, 122, 6689-6694; *Angew. Chem. Int. Ed.*, **2010**, 49, 6539-6544; n) J. Gao, J. Yan, S. G. Mitchell, H. N. Miras, A.G. Boulay, D.-L. Long, L. Cronin, *Chem. Sci.* **2011**, 2, 1502-1508; o) A. Lledó, S. Kamioka, A. C. Sather, J. Rebek, *Angew. Chem.* **2011**, 123, 1335-1337; *Angew. Chem. Int. Ed.* **2011**, 50, 1299-1301; p) W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg, J. R. Nitschke, *Angew. Chem.* **2011**, 123, 3541-3545; *Angew. Chem. Int. Ed.* **2011**, 50, 3479-3483; q) A. Granzhan, C. Schouwey, T. Riis-Johannessen, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2011**, 133, 7106-7115; r) M. Schmitt, M. Lal Saha, J. Fan, *Org. Lett.* **2011**, 13, 3916-3919; s) Y. Liu, C. Hu, A. Comotti, M. D. Ward, *Science* **2011**, 333, 436-440; t) A. Stephenson, S. P. Argent, T. Riis-Johannessen, I. S. Tidmarsh and M. D. Ward, *J. Am. Chem. Soc.* **2011**, 133, 858-870; u) C. R. K. Glasson, J. K. Clegg, J. C. McMurtrie, G. V. Meehan, L. F. Lindoy, C. A. Motti, B. Moubarak, K.S. Murray, J. D. Cashion, *Chem. Sci.* **2011**, 2, 540-543.
- [2] a) B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize, A. Van Dorsselaer, *Angew. Chem.* **1998**, 110, 3458-3461; *Angew. Chem. Int. Ed.* **1998**, 37, 3265-3268; b) V. Paraschiv, M. Crego-Calama, T. Ishi-i, C.J. Padberg, P. Timmerman, D.N. Reinhoudt, *J. Am. Chem. Soc.* **2002**, 124, 7638-7639; c) B. J. Holliday, Y.-M. Jeon, C. A. Mirkin, C. L. Stern, C. D. Incarvito, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, *Organometallics* **2002**, 21, 5713-5725; d) S. Tashiro, M. Tominaga, T. Kusukawa, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem.* **2003**, 115, 3389-3392; *Angew. Chem. Int. Ed.* **2003**, 42, 3267-3270; e) A. Hori, K. Yamashita, Makoto Fujita, *Angew. Chem.* **2004**, 116, 5126-5129; *Angew. Chem. Int. Ed.* **2004**, 43, 5016-5019; f) J. D. Badjic, S. J. Cantrill, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, 126, 2288-2289; g) J. T. Davis, M. S. Kaucher, F. W. Kotch, M. A. Iezzi, B. C. Clover, K. M. Mullaugh, *Org. Lett.* **2004**, 6, 4265-4268; h) A. Lohr, M. Lysetska, F. Würthner, *Angew. Chem.* **2005**, 117, 5199-5202; *Angew. Chem. Int. Ed.* **2005**, 44, 5071-5074; i) P. Mukhopadhyay, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2006**, 128, 14093-14102; j) M. Yamanaka, Y. Yamada, Y. Sei, K. Yamaguchi, K. Kobayashi, *J. Am. Chem. Soc.* **2006**, 128, 1531-1539; k) C. G. Claessens, M. J. Vicente-Arana, T. Torres, *Chem. Commun.* **2008**, 6378-6380; l) V. M. Cangelosi, T. G. Carter, L. N. Zakharov, D. W. Johnson, *Chem. Commun.* **2009**, 5606-5608; m) W. Jiang, A. Schäfer, P. C. Mohr, C. A. Schalley, *J. Am. Chem. Soc.* **2010**, 132, 2309-2320.
- [3] a) P. A. Jennings, P. E. Wright, *Science* **1993**, 262, 892-896; b) R. Pellarin, P. Schuetz, E. Guarnera, A. Caflisch, *J. Am. Chem. Soc.* **2010**, 132, 14960-14970.

- [4] Y. Sakata, S. Hiraoka, Mitsuhiko Shionoya, *Chem. Eur. J.* **2010**, *16*, 3318-3325.
- [5] a) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273-6283; b) A. Rang, M. Nieger, M. Engeser, A. Lützen, C. A. Schalley, *Chem. Commun.* **2008**, 4789-4791.
- [6] M. Fujita, F. Ibukuro, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 4175-4176.
- [7] P. J. Lusby, P. Müller, S. J. Pike, A. M. Z. Slawin, *J. Am. Chem. Soc.* **2009**, *131*, 16398-16400.
- [8] D. S. Black, G. B. Deacon, G. L. Edwards, *Aust. J. Chem.* **1994**, *47*, 217-227. Possible thermodynamic driving forces for the formation of *cis*-[(L²Pt)₂(4,4'-bipy)Cl₂] may include minimisation of the repulsive interaction between partial positively charged pyridyl donors (see Y.-R. Zheng, Z. Zhao, M. Wang, K. Ghosh, J. B. Pollock, T. R. Cook and P. J. Stang, *J. Am. Chem. Soc.* **2010**, *132*, 16873-16882.) and/or entropic factors related to desolvation upon lowering the dipole moment at the Pt centre (see F. Basolo and R. G. Pearson, *Mechanisms of inorganic reactions: a study of metal complexes in solution*, Wiley, London, **1967**).
- [9] The corresponding CSA salts are also stable in 1,1,2,2-tetrachlorethane at room temperature.